

ABSTRACT

The instant invention in one embodiment is a process for producing a nanocomposite polymer by dispersing a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material into a thermoplastic polymer. The process includes the step of mixing the polyvalent anionic polymer edge coated quaternary ammonium intercalated multi-layered silicate material with the thermoplastic polymer at a temperature greater than the melting point of the thermoplastic polymer. The instant invention in another embodiment is a process for producing a nanocomposite polymer by dispersing a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material into a thermoset polymer. The process of this embodiment includes the steps of: (a) mixing the polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material with a thermoset prepolymer; and (b) curing the thermoset prepolymer to set the thermoset polymer. The instant invention in yet another embodiment is a composition including: (a) a polymer; and (b) a multi-layered silicate material dispersed in the polymer, the multi-layered silicate material having edges, at least a portion of the edges of the multi-layered silicate material being bound to a polyvalent anionic organic material. The instant invention in further yet another embodiment is process for producing a nanocomposite polymer, including the steps of: (a) mixing a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material with a monomer; and (b) polymerizing the monomer.

NANOCOMPOSITE

This application claims the benefit of U.S. Provisional Application No. 60/108,979 filed November 18, 1998.

This invention relates to polymers reinforced with delaminated or exfoliated multi-layered silicates, that is, nanocomposite polymers.

Nanocomposite polymers are compositions comprising a relatively high number (but relatively low weight) of preferably single layers of exfoliated silicate material dispersed in a given volume of continuous polymer matrix, see United States Patent 5,717,000 to Seema V. Karande, Chai-Jing Chou, Jitka H. Solc and Kyung W. Suh, United States Patent Application Serial Number 10 034,620 filed December 31, 1996 and Giannelis, "Polymer Layered Silicate Nanocomposites", Advanced Materials, 1996, 8, No. 1, pages 29-35. As discussed in the '000 patent and as is well known in the art, nanocomposite polymers exhibit many increased physical property enhancements at a much lower weight percent of filler than conventionally filled polymers. Other patent literature disclosing nanocomposites include United States Patents 4,810,734, 4,558,075 and 3,516,959; as well as WO 93 04117 A and EP-A-0 459 472. Edge coating of multi-layer silicate material is known, see United States Patents 4,434,075 and 4,964,918.

However, it can be difficult to get the multi-layer silicate material to exfoliate into the polymer.

The instant invention is a solution, at least in part, to the above stated problem. In 20 one embodiment, the instant invention is a process for producing a nanocomposite polymer by dispersing a multi-layered silicate material into a thermoplastic polymer. The process comprises the step of mixing a quaternary ammonium intercalated multi-layered silicate material with the thermoplastic polymer at a temperature greater than the melting or softening point of the thermoplastic polymer, characterized by the quaternary ammonium intercalated multi-layered 25 silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material.

The instant invention in another embodiment is a process for producing a 30 nanocomposite polymer by dispersing a multi-layered silicate material into a thermoset polymer. The process of this embodiment comprises the steps of: (a) mixing a quaternary ammonium intercalated multi-layered silicate material with a thermoset prepolymer, characterized by the quaternary ammonium intercalated multi-layered silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are 35 bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material; and (b) curing the thermoset prepolymer to set the thermoset polymer.

producing a nanocomposite polymer, comprising the steps of: (a) mixing a quaternary ammonium intercalated multi-layered silicate material with a monomer, characterized by the quaternary ammonium intercalated multi-layered silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are 5 bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material; and (b) polymerizing the monomer.

Montmorillonite clay (a multi-layered silicate material) is stirred in water with an excess of 3,400 molecular weight sodium polyacrylate (a polyvalent anionic copolymer of mole 10 ration 1:1 of ethylene and acrylic acid) available from the Rhone-Poulenc Company to edge treat the clay. The edge treated clay is then stirred with an excess of a mixed quaternary ammonium compound (68 percent bis hydroxyethyl, dodecyl, methyl-quaternary ammonium compound and 32 percent bis hydroxy C-6 to C-9, dodecyl, methyl-quaternary ammonium compound) to produce a polyacrylate edge coated quaternary ammonium intercalated montmorillonite. The 15 polyacrylate edge coated quaternary ammonium intercalated montmorillonite is washed with water and dried. Ninety five parts of ethylene adipate thermoplastic polyurethane (available from The Dow Chemical Company) is melted (or softened) in a polymer mixer at 160 degrees Celsius at 200 rpm. Five parts of the dried polyacrylate edge coated quaternary ammonium intercalated montmorillonite, as described above in this paragraph, is added to the mixer and mixed for five 20 minutes. Transmission light microscopic examination of the product shows significantly fewer one hundred micrometer sized clay clusters relative to the use of non-edge coated material. Transmission electron microscopic examination of the product shows single and multiple layer exfoliation of the silicate layers of the montmorillonite. The layers are counted in a representative view. Most preferably, more of the layers are present as single layers than are present as 25 multiple layers. In any event the dispersion of the layers into the polymer is improved using the instant invention relative to the use of a non-edge-coated material.

Polyvalent anionic organic materials are organic chemicals that have more than one carboxylic acid or other anionic substituent such as a sulfonate or a phosphonate. Preferably, the polyvalent anionic organic material is a polyvalent anionic polymer. Most 30 preferably, the polyvalent anionic organic material is polyacrylic acid. However, the specific polyvalent anionic organic material used in the instant invention is not critical and can include, without limitation thereto, for example, copolymers of styrene and acrylic acid or styrene and sulfoethylmethacrylate.

The above referred to '000 patent and the '620 patent application list exemplary 35 multi-layered silicate materials required in the instant invention. For example, the multi-layered silicate material can be, without limitation thereto: montmorillonite; nontronite; beidellite; volkonskoite; hectorite saponite; sauconite; magadiite; medmontite; kenyait;

USSN 09/830,507

COMPLETE LISTING OF CLAIMS

1. (Original) A process for producing a nanocomposite polymer by dispersing a multi-layered silicate material into a thermoplastic polymer, comprising the step of mixing a quaternary ammonium intercalated multi-layered silicate material with the thermoplastic polymer at a temperature greater than the melting or softening point of the thermoplastic polymer, characterized by the quaternary ammonium intercalated multi-layered silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material.
5
- 10 2. (Original) The process of Claim 1, wherein the thermoplastic polymer is selected from the group consisting of a thermoplastic urethane, a thermoplastic epoxy, a thermoplastic polyester, a thermoplastic nylon, a thermoplastic polycarbonate; and blends thereof.
- 15 3. (Canceled)
4. (Canceled).
5. (Original) A process for producing a nanocomposite polymer by dispersing a multi-layered silicate material into a thermoset polymer, comprising the steps of:
 - 20 (a) mixing a quaternary ammonium intercalated multi-layered silicate material with a thermoset prepolymer, characterized by the quaternary ammonium intercalated multi-layered silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material;
 - 25 (b) curing the thermoset prepolymer to set the thermoset polymer.
6. (Original) The process of Claim 5, wherein the thermoset polymer is selected from the group consisting of a thermoset epoxy, a thermoset phenolic, a thermoset urethane, a thermoset rubber and blends thereof.
7. (Canceled)
8. (Canceled)

USSN 09/830,507

9. (Original) The process of Claim 1, wherein the thermoplastic polymer is selected from the group consisting of polypropylene, polyethylene, polystyrene, polystyrene copolymers, acrylic polymers, acetyl polymers and thermoplastic elastomers and blends thereof.

5 10. (Original) A composition comprising:

(a) a polymer; and

(b) a multi-layered silicate material dispersed in the polymer, the multi-layered silicate material having edges, characterized by at least a portion of the edges of the multi-layered silicate material being bound to a polyvalent anionic organic material.

10 11. (Original) The composition of Claim 10, wherein at least about one half of the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material.

15 12. (Original) The composition of Claim 10 or Claim 11, wherein the polymer is selected from the group of thermoplastic polymers and thermoset polymers and blends thereof.

13. (Original) The composition of Claim 12, wherein the thermoplastic polymers and thermoset polymers are selected from the group consisting of a thermoplastic urethane, a thermoplastic epoxy, a thermoplastic polyester, a thermoplastic nylon, a thermoplastic polycarbonate, polypropylene, polyethylene, polystyrene, polystyrene copolymers, acrylic polymers, acetyl polymers, thermoplastic elastomers, thermoset epoxy, a thermoset phenolic, a thermoset urethane, a thermoset rubber and blends thereof.

20 14. (Currently Amended) The process of Claim 4, 8 or 9, wherein the polyvalent anionic organic material is a polyacrylate.

15. (Previously Amended) The composition of Claim 13, wherein the polyvalent anionic organic material is a polyacrylate.

16. (Original) A process for producing a nanocomposite polymer, comprising the steps of:

(a) mixing a quaternary ammonium intercalated multi-layered silicate material with a monomer, characterized by the quaternary ammonium intercalated multi-layered silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material; and

(b) polymerizing the monomer.

USSN 09/830,507

17. (Original) The process of Claim 16, wherein the monomer is a blend of monomers.

18. (Original) The process of Claim 16, wherein the polymer is selected from the group consisting of a thermoplastic urethane, a thermoplastic epoxy, a thermoplastic 5 polyester, a thermoplastic nylon, a thermoplastic polycarbonate, polypropylene, polyethylene, polystyrene, polystyrene copolymers, acrylic polymers, acetyl polymers, thermoplastic elastomers, thermoset epoxy, a thermoset phenolic, a thermoset urethane, a thermoset rubber and blends thereof.

19. (Original) The process of Claim 18, wherein the polyvalent anionic organic 10 is a polyacrylate.

C- 44407

Received in the U.S. Patent and Trademark Office:

Reply to Advisory Action

Abstract

Page 1 and 2 of Specification

Complete Listing of Claims

Notice of Appeal (plus 2 copies)

Postcard

Applicant: Chou, et al.

Serial No.: 09/830,507

Filed: June 15, 2001

Title: NANOCOMPOSITE

NCD/blw Mailed 08/05/03